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MACROCYCLES CONTAINING TIN. TWO SYNTHESES OF 1,1,6,6,11,11,16,1--ETC(U)
SEP 82 M NEWCOMB, Y AZUMA, A R COURTNEY N00014-79-C-0584
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Synthesis
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Synthetic techniques and methods for analysis and purification of macrocycles containing tin atoms are exemplified by the title syntheses. Highlights of the syntheses include a highly selective conversion of 1,4-bis-(triphenylstannyl)butane to 1,4-bis-(bromodiphenylstannyl)butane and a two component macrocyclization which proceeds in 43% yield to give the 20-membered ring product. Analytical HPLC and preparative chromatography methods for characterization and purification of the macrocycles and their synthetic intermediates

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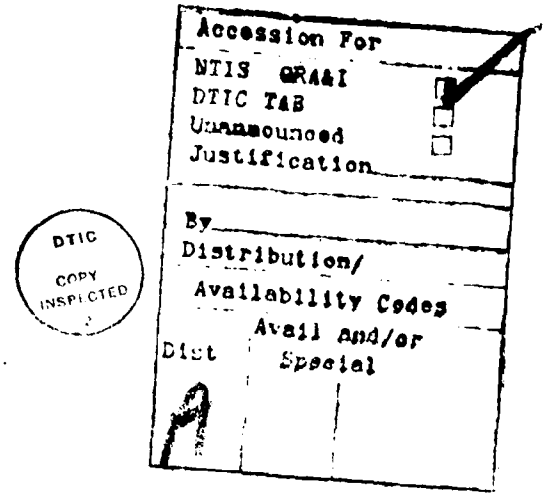
and analogs are described. Other syntheses which show the generality of the methods are discussed.



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TECHNICAL REPORT NO. 3

Macrocycles Containing Tin.

Two Syntheses of

1,1,6,6,11,11,16,16-Octaphenyl-1,6,11,16-tetrastannacycloeicosane

and a Synthesis of

1,1,6,6-Tetraphenyl-1,6-distannacyclodecane

by

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Sept. 22, 1982

Macrocycles Containing Tin. Two Syntheses of 1,1,6,6,11,11,16,16-Octaphenyl-1,6,11,16-tetrastannacycloeicosane and a Synthesis of 1,1,6,6-Tetraphenyl-1,6-distannacyclodecane

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Summary: The title syntheses are described. The synthetic and purification and analytical methods employed are of general utility for the preparation and functionalization of members of this class of compounds.

Macrocyclic, polydentate cation-complexing ligands (crown ethers, cryptands, etc.) have enjoyed a broad and useful chemistry during the past decade and a half, but their counterparts, anion-complexing macrocycles have received relatively little attention. Recent advances in anion complexation, including structural selectivity, by macrocyclic polyammonium ligands suggest that this will be a fertile area of study.[2] Reasoning that polystanna macrocycles may be appropriately substituted to give Lewis acid complexing ligands which are direct analogs of crown ethers or cryptands, we have developed synthetic procedures for this class of compounds represented by the title compound (1). Two approaches (Scheme) have yielded the target 20-membered ring compound. The synthetic methods and purification techniques described herein are generally applicable for this class of compounds and also furnish tin functionalized macrocycles. We are unaware of other neutral macrocycles with the potential for anion complexation.

All reactions were run in argon or nitrogen atmospheres. Treatment of the diGrignard reagent from 1,4-dibromobutane with triphenylstannyl chloride in tetrahydrofuran (THF) gave 1,4-bis-(triphenylstannyl)-butane[3a,b] (2, mp 148.5-149 °C) in 77% isolated yield after recrystallization from hexane--dichloromethane (2:1, v:v). Unacceptably low selectivity was observed in several attempted conversions of 2 to 1,4-bis-(bromodiphenylstannyl)butane (3) with various reagents and conditions; a second phenyl group was readily replaced giving the dibromophenylstannyl moiety. However, treatment of 2 with 2.1 molar equivalents of hydrogen bromide in dry dichloromethane at -78 °C followed by slow warming to room temperature gave, after recrystallization (dry ether), 3[3a] in 75% yield (mp 88-90 °C). The dibromide 3 was treated with excess 4-chlorobutylmagnesium bromide in THF at -10 °C for 1.5 h followed by warming to room temperature (7 h) to give 1,14-dichloro-5,5,10,10-tetraphenyl-5,10-distannatetradecane (1)[3a] which was purified by reverse phase chromatography (C-18, methanol elution) in 62% yield (oil).

The two component macrocyclization was accomplished at high dilution. The dibromide 3 was added to excess lithium metal in THF to give the dilithium reagent 5 (total base = 63% of theory). A THF solution of 5 (diluted to 0.037 M) was added slowly (2 h) to a THF solution of 4 (1.0 molar equivalent, 0.02 M) at 0 °C followed by warming to room temperature (12 h). After a conventional work-up, the crude product was purified by reverse phase chromatography (C-18) with THF--acetonitrile elution (1:3, v:v) to give the desired macrocycle 1[3] in 43% isolated yield (mp 107.5-108 °C from hexane--ether, 3:1).

Alternatively, macrocycle 1 was also obtained in lower yield from a high dilution, four component macrocyclization reaction. Thus, the diGrignard reagent from 1,4-dibromobutane in THF (0.07 M) was added over 2 h to one molar equivalent of dibromide 3 in THF (0.034 M) at 0 °C. After 12 h at room temperature, the reaction was quenched and worked up. The crude products were purified by preparative reverse phase chromatography as above to give, after recrystallization, the desired macrocycle 1 in 16% yield and 1,1,6,6-tetraphenyl-1,6-distannacyclodecane[3a,b] (6, mp 114-114.5 °C, lit.[4] mp 96-98 °C) in 10% yield. Compound 6 has been prepared by a different route.[4]

The macrocycles 1 and 6 may be analyzed readily by analytical HPLC (reverse phase, C-18) with methanol elution; the 10-membered ring compound 6 elutes before 1. However, for preparative chromatography, the solubilities of 1 and 6 in methanol are inconveniently low. Thus, chromatography with the mixed solvent system THF--acetonitrile was developed. We found that analytical HPLC on 10 μ Spherisorb ODS columns correlated well with preparative chromatography on 40 μ ODS supplied by J. T. Baker Co.; the analytical phase retained material about 1.5 times as long as the preparative phase in terms of column volumes.

The procedures described above are generally useful for the preparation and functionalization of other tin containing macrocycles. For example, the reactions of the 6-, 8-, and 10-carbon analogs of 3 with the corresponding chain length α,ω-diGrignard reagents gave the 14-, 18-, and 22-membered ring analogs of the distanna compound 6, respectively, as well as low yields of the 28-, 36-, and 44-membered ring analogs of tetrastanna compound 1, respectively. All separations were accomplished by reverse phase chromatography. Further, when the selective bromination procedure was applied to macrocycle 6, we obtained 1,6-dibromo-1,6-diphenyl-1,6-distannacyclodecane;[3a] this reaction exemplifies a critically important functionalization of the macrocycles. Finally, preparative reverse phase chromatography of the intermediate tin bromides is also possible on a C-18 column with THF--acetonitrile elution if dry solvents are used.

As in any macrocyclization reaction, the high dilution methods we used required careful technique. However, in our minds, the key steps to obtaining macrocycle 1 were the selective bromination of 2 and our development of a preparative chromatography method. The two component macrocyclization route and reverse phase preparative chromatography permit the synthesis of 1 in gram batches. With the methods at hand we plan to prepare and functionalize several members of this class of compounds and explore their application in anion coordination chemistry.

Acknowledgement: This work was supported by the Office of Naval Research.

References and Notes

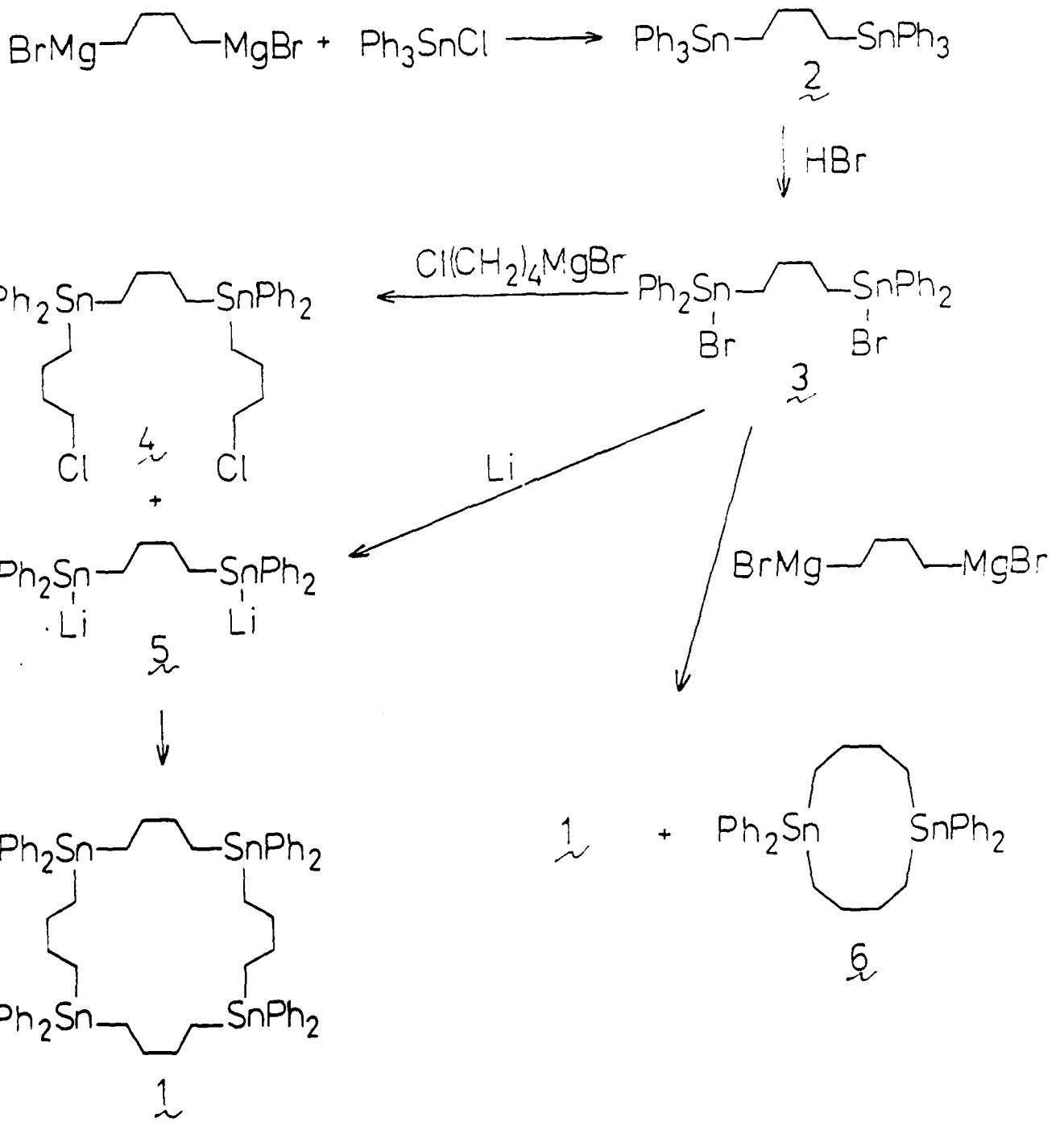
(1) Camille and Henry Dreyfus Teacher-Scholar, 1980-1985.

(2) Dietrich, B.; Hosseini, M. W.; Lehn, J. M.; Sessions, R. B. J. Am. Chem. Soc. 1981, 103, 1282; Hosseini, M. W.; Lehn, J. M. J. Am. Chem. Soc. 1982, 104, 3525; and references in each.

(3) (a)The compound was characterized by ^{1}H NMR spectroscopy; (b) the compound was characterized by ^{1}H-decoupled ^{13}C NMR spectroscopy and by osmometric molecular weight determination; (c) a satisfactory elemental analysis (±0.4% for C, H) was obtained.

(4) Davies, A. G.; Tse, M. -W.; Kennedy, J. D.; McFarlane, W.; Pyne, G. S.; Ladd, M. F. C.; Povey, D. C. J. Chem. Soc., Chem. Commun. 1978, 791.

Scheme


BrMg MgBr + Ph3SnCl
Ph3Sn SnPh3
2
HBr
Cl(CH2)4MgBr
Ph2Sn SnPh2
Br Br
3
Ph2Sn SnPh2
Cl Cl
4
+
Li
Ph2Sn SnPh2
Li Li
5
BrMg MgBr
Ph2Sn SnPh2
Ph2Sn SnPh2
1
1 + Ph2Sn SnPh2
6

Supplementary Information for Review Purposes

Osmometric Molecular Weight Determinations.

Compound	MW Calcd	MW Found
2	755	734
1	1315	1341
6	657	654

Elemental Analysis of Compound 1.

$C_{64}H_{72}Sn_4$: %C calcd 58.38, found 58.06; %H calcd 5.52, found 5.43.

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